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Supplementary material for the paper entitled:

A Conformational Study of Peptides with the General Structure Ac-L-Xaa-Pro-D-Xaa-L-Xaa-NH_2: Spectroscopic Evidence for a Peptide with Significant β-Turn Character in Water and in Dimethyl Sulfoxide

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This supplementary material contains a complete listing of the spectroscopic characterization of all peptides examined. Routine FT ^1H NMR spectra were obtained at 500 MHz and ^{13}C at 125 MHz on a Bruker Model AM-500 spectrometer. Chemical shifts are reported as δ units ppm relative to DMSO-d_6 (2.49 ppm) for ^1H and (39.5 ppm) for ^{13}C in DMSO-d_6 as solvent and DMSO (2.73 ppm) as an internal standard in 10% D_2O/90% H_2O solutions at 5° C, pH= 3.6 ± 0.6. High resolution mass spectrometry was performed at the Southern California Mass Spectrometry Facility, University of California, Riverside on a ZAB instrument in fast atom bombardment mode. The purity of each peptide was assessed to be >95% by thin layer chromatography (TLC) and High Pressure Liquid Chromatography (HPLC). TLC was carried out using EM Reagents hard TLC plates with fluorescent indicator (SiO_2 60, F-254) with the following eluent systems: A. *n*-butanol: acetic acid: water (4:1:1) and B. *n*-butanol: acetic acid: water: ethyl acetate (1:1:1:1). TLC plates were visualized with I_2 vapors, UV lamps, or by exposure to Cl_2 vapors followed by treatment with a solution of *o*-tolidine in acetic acid with KI.

Details pertaining to the acquisition of the ROESY spectra can be found in the paper.

Ac-Val-Pro-D-Ser-His-NH_2

^1H NMR (DMSO-d_6) δ: 8.95 His-ε (s, 1H), 8.53 Ser-NH (d, 1H), 8.05 Val-NH (d, 1H), 8.01 His-NH (d, 1H), 7.35 Cap-NH (s, 1H), 7.27 His-δ & Cap-NH (m, 2H), 4.42 His-α (m, 1H), 4.34 Pro-α (m, 1H), 4.20 Val-α (m, 1H), 4.17 Ser-α (m, 1H), 3.86 Pro-δ (m, 1H), 3.71 Ser-β (m, 1H), 3.65 Ser-β (m, 1H), 3.60 Pro-δ (m, 1H), 3.22 His-β (m,1H), 3.00 His-β (m, 1H), 2.05 Pro-β (m, 1H), 1.98 Pro-γ (m,1H), 1.82 Pro-γ (m, 1H), 1.82 Ac-cap (s, 3H), 1.80 Pro-β (m, 1H), 1.75 Val-β (m, 1H), 0.90 Val-γ (m, 6H).

^1H NMR (10% D_2O/90% H_2O) δ: 8.70 Ser-NH (d, 1H), 8.50 His-NH & His-ε (m, 2H), 8.25 Val-NH (d, 1H), 7.52 Cap-NH (s, 1H), 7.21 Cap-NH (s, 1H), 7.15 His-δ (s, 1H), 4.60 His-α (m, 1H), 4.38 Pro-α (m, 1H), 4.32 Ser-α (m, 1H), 4.23 Val-α (m, 1H), 3.85 Pro-δ (m, 1H), 3.75 Ser-β (m, 1H), 3.67 Ser-β (m, 1H), 3.55 Pro-δ (m, 1H), 3.22 His-β (m,1H), 3.00 His-β (m, 1H), 2.21

Pro-β, (m, 1H), 2.00 Pro-γ (m, 1H), 1.90 Pro-γ (m, 1H), 1.88 Ac-cap (s, 3H), 1.85 Pro-β (m, 1H), 1.82 Val-β (m, 1H), 0.83 Val-γ (d, 3H), 0.80 Val-γ (d, 3H).

^{13}C NMR (DMSO-d_6) δ: 172.2, 171.8, 171.5, 170.7, 169.1 133.0, 129.9, 116.6, 61.1, 60.0, 56.1, 55.3, 51.8, 47.5, 30.0, 29.1, 26.3, 24.5, 22.1, 18.7.

Calc. for $[MH]^+$ $C_{21}H_{34}N_7O_6$ [480.2570]; Obs. [480.2586]. TLC (B) R_f 0.44.

Ac-Val-Pro-D-Ala-His-NH$_2$

^{1}H NMR (DMSO-d_6) δ: 8.95 His-ε (s, 1H), 8.37 Ala-NH (d, 1H), 7.95 His-NH (d, 1H), 7.90 Val-NH (d, 1H), 7.29 Cap-NH (s, 1H), 7.27 His-δ (s, 1H), 7.23 Cap-NH (s, 1H), 4.44 His-α (m, 1H), 4.22 Val-α (m, 1H), 4.20 Pro-α (m, 1H), 4.17 Ala-α (m, 1H), 3.84 Pro-δ (m, 1H), 3.56 Pro-δ (m, 1H), 3.21 His-β (m,1H), 2.96 His-β (m, 1H), 2.08 Pro-β (m, 1H), 1.95 Pro-γ (m,1H), 1.84 Pro-γ (m, 1H), 1.82 Ac-cap (s, 3H), 1.78 Pro-β & Val-β (m, 2H), 1.16 Ala-β (d, 3H), 0.82 Val-γ (d, 6H).

^{1}H NMR (10% D_2O/90% H_2O) δ: 8.71 Ala-NH (d, 1H), 8.62 His-ε (s, 1H), 8.56 His-NH (d, 1H), 8.36 Val-NH (d, 1H), 7.71 Cap-NH (s, 1H), 7.33 Cap-NH (s, 1H), 7.30 His-δ (s, 1H), 4.67 His-α (m, 1H), 4.38 Pro-α (m, 1H), 4.36 Val-α (m, 1H),4.27 Ala-α (m, 1H), 3.96 Pro-δ (m, 1H), 3.69 Pro-δ (m, 1H), 3.35 His-β (m, 1H), 3.13 His-β (m, 1H), 2.31 Pro-β (m, 1H), 2.09 Pro-γ (m, 1H), 2.00 Pro-γ, Val-β, & Ac-cap (m, 5H), 1.90 Pro-β (m, 1H), 1.30 Ala-β (d, 3H), 0.97 Val-γ (d, 3H), 0.93 Val-γ (d, 3H).

^{13}C NMR (DMSO-d_6) δ: 171.86, 171.66, 171.64, 170.68, 169.22, 133.48, 129.87, 116.63, 60.09, 56.05, 51.65, 48.25, 47.41, 29.65, 29.07, 26.60, 24.62, 22.12, 18.75, 18.64, 17.25.

Calc. for $[MH]^+$ (Low Res.) $C_{21}H_{34}N_7O_5$ [464]; Obs. [464]. TLC (B) R_f 0.35.

Ac-Val-Pro-D-Ser-Phe-NH$_2$

^{1}H NMR (DMSO-d_6) δ: 8.24 Ser-NH (d, 1H, J = 8.1 Hz), 8.07 Val-NH (d, 1H, J = 8.3 Hz), 7.90 Phe-NH (d, 1H, J = 8.8 Hz), 7.28 Cap-NH (s, 1H), 7.18 Phe-ring & Cap-NH (m, 6H), 4.33 Phe-α & Pro-α (m, 2H), 4.23 Val-α (m, 1H), Ser-α 4.17 (m, 1H), 3.85 Pro-δ (m, 1H), 3.52 Pro-δ & Ser-β (m, 3H), 3.07 Phe-β (m, 1H), 2.85 Phe-β (m, 1H), 2.04 Pro-β (m, 1H), 1.95 Pro-γ (m, 1H), 1.86 Pro-β, Pro-γ & Val-β (m, 3H), 1.83 Ac-cap (s, 3H), 0.86 Val-γ (d, 3H), 0.82 Val-γ (d, 3H).

^{1}H NMR (10% D_2O/90% H_2O) δ: 8.46 Ser-NH (d, 1H, J = 8.1 Hz), 8.28 Phe-NH (d, 1H, J = 7.3 Hz), 8.14 Val-NH (d, 1H, 7.8), 7.59 Cap-NH (s, 1H), 7.33 Phe-ring (m, 5H), 7.09 Cap-NH (s, 1H), 4.58 Phe-α (m, 1H), 4.45 Pro-α (m, 1H), 4.39 Val-α & Ser-α (m, 2H), 3.94 Pro-δ (m, 1H), 3.71 Pro-δ & Ser-β (m, 3H), 3.23 Phe-β (m, 1H), 3.01 Phe-β (m, 1H), 2.30 Pro-β (m, 1H), 2.05 Pro-γ & Val-β (m, 3H), 2.02 Ac-cap (s, 3H), 1.95 Pro-β (m, 1H), 1.00 Val-γ (d, 3H), 0.94 Val-γ (d, 3H).

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^{13}C NMR (DMSO-d_6) δ: 172.7, 171.8, 170.6, 169.5, 169.2, 138.3, 129.1, 127.9, 126.0, 61.2, 59.8, 56.0, 54.9, 54.3, 47.3, 37.2, 29.8, 29.0, 24.6, 22.1, 18.9, 18.7.

Calc. for $[MH]^+$ $C_{24}H_{36}N_5O_6$ [490.2666]; Obs. [490.2674]. TLC (B) R_f 0.50.

Ac-Val-Pro-D-Ser-Ile-NH$_2$

^{1}H NMR (DMSO-d_6) δ: 8.01 Ser-NH (d, 1H, J = 7.7 Hz), 7.99 Val-NH (d, 1H, J = 7.3 Hz), 7.24 Ile-NH (d, 1H) 7.16 Cap-NH (s, 1H), 7.00 Cap-NH (s, 1H), 4.18 Pro-α (m, 1H) 4.16 Ser-α (m, 1H), 4.15 Val-α (m, 1H), 4.04 Ile-α (m, 1H), 3.4 Pro-δ (m, 1H) 3.30 Pro-δ & Ser-β (m, 3H), 2.03 Pro-β (m, 1H), 1.95 Pro-γ (m, 2H), 1.92 Ac-cap (s, 3H), 1.90 Val-β & Pro-β (m, 2H) 1.87 Ile-β (m, 1H), 1.18 Ile-γ1 (m, 1H), 1.03 Ile-γ1 (m, 1H), 0.94-90 Val-γ, Ile-γ2, & Ile-δ (m, 12H).

^{1}H NMR (10% D_2O/90% H_2O) δ: 8.20 Ser-NH (d, 1H), 7.85 Cap-NH (s, 1H), 7.65 Val-NH (d, 1H), 7.35 Ile-NH (d, 1H), 7.27 Cap-NH (s, 1H), 4.49 Ser-α (m, 1H), 4.47 Pro-α (m, 1H) 4.38 Val-α (m, 1H), 4.22 Ile-α (m, 1H), 3.99 Pro-δ (m, 1H), 3.90 Ser-β (m, 2H), 3.70 Pro-δ (m, 1H), 2.32 Pro-β (m, 1H), 2.05 Pro-γ (m, 2H), 2.02 Ac-cap (s, 3H), 1.95 Pro-β, Val-β, & Ile-β (m, 3H), 1.42 Ile-γ1 (m, 1H), 1.21 Ile-γ1 (m, 1H), 1.00 Val-γ (d, 3H), 0.98 Val-γ & Ile-γ2 (m, 6H), 0.88 Ile-δ (m, 3H).

^{13}C NMR (DMSO-d_6) δ: 172.7, 171.7, 170.4, 169.5, 169.2, 61.5, 59.6, 57.0, 56.0, 54.9, 47.2, 36.3, 29.8, 29.1, 24.5, 24.0, 22.1, 19.0, 18.6, 15.4, 10.9.

Calc. for $[MH]^+$ $C_{21}H_{38}N_5O_6$ [456.2822]; Obs. [456.2820]. TLC (A) R_f = 0.65

Ac-Val-Pro-D-Ala-Phe-NH$_2$

^{1}H NMR (DMSO-d_6) δ: 8.11 Ala-NH (d, 1H, J = 7.8 Hz), 8.08 Val-NH (d, 1H, J = 8.4 Hz), 8.03 Phe-NH (d, 1H, J = 8.6 Hz), 7.37 Cap-NH (s, 1H), 7.26 Phe-ring (m, 5H), 7.16 Cap-NH (s, 1H), 4.35 Phe-α (m, 1H), 4.27 Val-α & Pro-α (m, 2H), 4.23 Ala-α (m, 1H), 3.84 Pro-δ (m, 1H), 3.60 Pro-δ (m, 1H), 3.11 Phe-β (m, 1H), 2.84 Phe-β (m, 1H), 1.87 Ac-cap, Pro-β, Pro-γ, & Val-β (m, 8H), 1.05 Ala-β (d, 3H, J = 7.0 Hz), 0.91 Val-γ (d, 3H, J = 6.5 Hz), 0.87 Val-γ (d, 3H, J = 6.6 Hz).

^{1}H NMR (10% D_2O/90% H_2O) δ: 8.54 Ala-NH (d, 1H, J = 6.5 Hz), 8.37 Phe-NH (d, 1H, J = 7.3 Hz), 8.30 Val-NH (d, 1H, J = 7.3 Hz), 7.65 Cap-NH (s, 1H), 7.40 Phe-ring (m, 2H), 7.30 Phe-ring (m, 3H), 7.20 Cap-NH (s, 1H), 4.57 Phe-α (m, 1H), 4.38 Val-α (m, 1H), 4.36 Pro-α (m, 1H), 4.22 Ala-α (m, 1H), 3.96 Pro-δ (m, 1H), 3.71 Pro-δ (m, 1H), 3.25 Phe-β (m, 1H), 3.00 Phe-β (m, 1H), 2.29 Pro-β (m, 1H), 2.1-1.95 Pro-γ & Val-β(m, 3H), 2.0 Ac-cap (s, 3H), 1.91 Pro-β (m, 1H) 1.17 Ala-β (d, 3H), 0.99 Val-γ (d, 3H), 0.91 Val-γ (d, 3H).

^{13}C NMR (DMSO-d_6) δ: 172.9, 171.5, 171.2, 170.6, 169.2, 138.3, 129.1, 127.9, 126.1, 59.9, 55.9, 54.1, 47.9, 47.32, 37.3, 29.8, 29.1, 24.6, 22.2, 19.0, 18.7, 17.8.

Calc. for $[MH]^+$ $C_{24}H_{36}N_5O_5$ [474.2716]; Obs. [474.2706]. TLC (A) R_f = 0.57

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Ac-Ala-Pro-D-Val-His-NH_2

^1H NMR (DMSO-d_6) δ: 8.95 His-ε (s, 1H), 8.22 Ala-NH (d, 1H, J = 7.3 Hz), 8.09 His-NH (d, 1H, J = 7.0 Hz), 8.0 Val-NH (d, 1H J = 7.3 Hz), 7.28 Cap-NH (s, 1H), 7.25 His-δ (s, 1H), 7.22 Cap-NH (s, 1H), 4.50 Ala-α (m, 1H), 4.49 His-α (m, 1H), 4.35 Pro-α (m, 1H), 3.78 Val-α (m, 1H), 3.65 Pro-δ (m, 1H), 3.52 Pro-δ (m, 1H), 3.20 His-β (m, 1H), 2.95 His-β (m, 1H), 2.05 Pro-β (m, 1H), 1.92 Val-β & Pro-γ (m, 2H), 1.85 Pro-γ (m, 1H), 1.80 Ac-cap (s, 3H), 1.75 Pro-β (m, 1H), 1.11 Ala-β(d, 3H), 0.7 Val-γ (d, 3H), 0.62 Val-γ (d, 3H).

^1H NMR (10% D_2O/90% H_2O) δ: 8.85 His-NH (d, 1H, J = 8.1 Hz), 8.54 His-ε (s, 1H), 8.46 Val-NH (d, 1H, J = 7.4 Hz), 8.39 Ala-NH (d, 1H, J = 5.3 Hz), 7.67 Cap-NH (s, 1H), 7.36 Cap-NH (s, 1H), 7.33 His-δ (s, 1H), 4.76 His-α (m, 1H), 4.53 Ala-α (m, 1H), 4.49 Pro-α (m, 1H), 4.08 Val-α (m, 1H), 3.85 Pro-δ (m, 1H) 3.68 Pro-δ (m, 1H), 3.40 His-β (m, 1H), 3.17 His-β (m, 1H), 2.32 Pro-β (m, 1H), 2.07 Pro-γ (m, 2H) 1.99 Ac-cap (s, 3H), 1.90 Val-β & Pro-β (m, 2H), 1.32 Ala-β (d, 3H) 0.8 Val-γ (d, 3H), 0.71 Val-γ (d, 3H).

^{13}C NMR (DMSO-d_6) δ: 172.2, 171.9, 171.2, 170.8, 168.7, 133.7, 130.1, 117.1, 59.7, 58.2, 51.7, 46.8, 46.0, 29.3, 29.1, 27.0, 24.6, 22.2, 18.9, 17.6, 16.8.

Calc. for $[MH]^+$ $C_{21}H_{34}N_7O_5$ [464.2621]; Obs. [464.2598]. TLC (A) R_f = 0.30.

Ac-*tert*-Leu-Pro-D-Ala-His-NH_2

^1H NMR (DMSO-d_6) δ: 8.07 Ala-NH (d, 1H, J = 7.0 Hz), 7.98 His-NH (d, 1H, J = 8.2 Hz), 7.92 *t*-Leu-NH (d, 1H, J = 8.9 Hz), 7.53 His-ε (s, 1H), 7.25 Cap-NH (s, 1H), 7.07 Cap-NH (s, 1H), 6.76 His-δ (s, 1H), 4.53 *t*-Leu-α (d, 1H, J = 8.9 Hz), 4.36 Pro-α & His-α (m, 2H), 4.26 Ala-α (m, 1H), 3.76 Pro-δ (m, 1H), 3.65 Pro-δ (m, 1H), 3.00 His-β (m, 1H), 2.83 His-β (m, 1H), 2.06 Pro-β (m, 1H), 1.87 Pro-β, Pro-γ & Ac-cap (m, 6H), 1.14 Ala-β (d, 3H, J = 7.0 Hz), 0.97 *t*-Leu-γ (s, 9H).

^1H NMR (10% D_2O/90% H_2O) δ: 8.63 His-ε (s, 1H), 8.59 Ala-NH (d, 1H), 8.56 His-NH (d, 1H), 8.16 *t*-Leu-NH (d, 1H), 7.70 Cap-NH (s, 1H), 7.36 His-δ (s, 1H), 7.31 Cap-NH (s, 1H), 4.61 His-α (m, 1H), 4.50 *t*-Leu-α (d, 1H), 4.40 Pro-α (m, 1H), 4.25 Ala-α (m, 1H), 3.95 Pro-δ (m, 1H), 3.66 Pro-δ (m, 1H), 3.37 His-β (m, 1H), 3.17 His-β (m, 1H), 2.10 Pro-β (m, 1H), 2.08 Pro-γ (m, 1H), 2.06 Ac-cap (s, 3H), 1.98 Pro-γ (m, 1H), 1.92 Pro-β (m, 1H), 1.29 Ala-β (d, 3H), 1.01 *t*-Leu-γ (s, 9H).

^{13}C NMR (DMSO-d_6) δ: 171.9, 171.4, 168.9, 168.6, 168.1, 129.5, 116.2, 57.3, 51.3, 50.4, 47.9, 47.3, 46.1, 33.8, 28.8, 25.9, 25.1, 24.1, 21.8, 17.2, 16.2.

Calc. for $[MH]^+$ (Low Res.) $C_{22}H_{36}N_7O_5$ [478]; Obs. [478]. TLC (A) R_f = 0.36.

Ac-Ala-Pro-D-Ala-Phe-NH_2

^1H NMR (DMSO-d_6) δ: 8.15 L-Ala-NH (d, 1H, J = 7.3 Hz), 8.09 D-Ala-NH (d, 1H, J = 7.6 Hz), 8.04 Phe-NH (d, 1H, J = 8.7 Hz), 7.36 Cap-NH (s, 1H), 7.25 Phe-ring (m, 5H), 7.12 Cap-NH (s, 1H), 4.53 L-Ala-α (m, 1H), 4.38 Phe-α (m, 1H), 4.27 Pro-α (m, 1H), 4.18 D-Ala-α (m, 1H), 3.69 Pro-δ (m, 1H), 3.58 Pro-δ (m, 1H), 3.11 Phe-β (m, 1H), 2.84 Phe-β (m, 1H), 2.08 Pro-β (m,

1H), 1.96 Pro-γ (m, 1H), 1.84 Ac-Cap & Pro β,γ (m, 5H), 1.18 L-Ala-β (d, 3H, J = 6.9 Hz), 1.05 D-Ala-β (d, 3H, J = 7.8 Hz).

^{1}H NMR (10% D_2O/90% H_2O) δ: 8.57 D-Ala-NH (d, 1H), 8.40 L-Ala-NH (d, 1H), 8.39 Phe-NH (d, 1H) 7.66 Cap-NH (s, 1H), 7.37 Phe-ring (m, 2H), 7.31 Phe-ring (m, 1H), 7.27 Phe-ring (m, 2H), 7.23 Cap-NH (s, 1H), 4.56 Phe-α (m, 1H), 4.54 L-Ala-α (m, 1H), 4.40 Pro–α (m, 1H), 4.22 D-Ala-α (m, 1H), 3.85 Pro-δ (m, 1H), 3.65 Pro-δ (m, 1H), 3.25 Phe-β (m, 1H), 3.00 Phe-β (m, 1H), 2.30 Pro-β (m, 1H), 2.08 Pro-γ (m, 2H), 1.98 Ac-cap (s, 3H), 1.90 Pro-β (m, 1H) 1.34 L-Ala-β (d, 3H), 1.18 D-Ala-β (d, 3H).

^{13}C NMR (DMSO-d_6) δ: 172.9, 171.6, 171.5, 171.2, 168.8, 138.3, 129.2, 127.9, 126.1, 59.9, 54.1, 48.2, 46.8, 46.1, 37.3, 28.9, 24.6, 22.3, 17.6, 16.8.

Calc. for $[MH]^+$ $C_{22}H_{32}N_5O_5$ [446.2403]; Obs. [446.2408]. TLC (A) R_f = 0.51.

Ac-Ala-Pro-Gly-Phe-NH$_2$

^{1}H NMR (DMSO-d_6) δ: 8.21 Gly-NH (t, 1H, J = 5.6 Hz), 8.16 Ala-NH (d, 1H, J = 7.4 Hz), 7.90 Phe-NH (d, 1H, J = 8.5 Hz), 7.36 Cap-NH (s, 1H), 7.25 Phe-ring (m, 5H), 7.18 Cap-NH (s, 1H), 4.55 Ala-α (m, 1H), 4.41 Phe-α (m, 1H), 4.28 Pro-α (m, 1H), 3.75-3.42 Pro-δ & Gly-α (m, 4H), 3.09 Phe-β (m, 1H), 2.85 Phe-β (m, 1H), 2.07 Pro-β (m, 1H), 1.95 Pro-γ (m, 1H), 1.84 Ac-cap & Pro-γ, β (m, 5H), 1.18 Ala-β (d, 3H, J = 6.87 Hz).

^{1}H NMR (10% D_2O/90% H_2O) δ: 8.60 Gly-NH (dd, 1H), 8.40 Phe-NH (d, 1H), 8.22 Ala-NH (d, 1H), 7.70 Cap-NH (s, 1H), 7.40 Phe-ring (m, 2H), 7.32 Phe-ring (m, 1H), 7.22 Phe-ring (m, 2H), 7.18 Cap-NH (s, 1H), 4.59 Ala-α (m, 1H), 4.57 Phe-α (m, 1H), 4.40 Pro-α (m, 1H), 3.90 Gly-α (dd, 1H), 3.86 Pro-δ (m, 1H), 3.84 Gly-α (dd, 1H), 3.68 Pro-δ (m, 1H), 3.20 Phe-β (m, 1H), 3.05 Phe-β (m, 1H), 2.30 Pro-β (m, 1H), 2.06 Pro-γ (m, 2H), 2.01 Ac-cap (s, 3H), 1.85 Pro-β (m, 1H), 1.33 Ala-β (d, 3H).

^{13}C NMR (DMSO-d_6) δ: 172.7, 172.0, 171.0, 168.7, 168.4, 138.0, 129.0, 127.9, 126.1, 59.9, 53.9, 46.7, 45.9, 42.0, 37.3, 28.9, 24.4, 22.1, 16.5.

Calc. for $[MH]^+$ $C_{21}H_{30}N_5O_5$ [432.2247]; Obs. [432.2250]. TLC (A) R_f = 0.70.

Ac-Ala-Pro-D-Val-Phe-NH$_2$

^{1}H NMR (DMSO-d_6) δ: 8.24 Phe-NH (d, 1H, J = 8.7 Hz), 8.14 Ala-NH (d, 1H, J = 7.5 Hz), 7.72 Val-NH (d, 1H, J = 8.6 Hz), 7.36 Cap-NH (s, 1H), 7.26 Phe-ring (m, 4H), 7.18 Phe-ring (m, 1H), 7.14 Cap-NH (s, 1H), 4.55 Ala-α (m, 1H), 4.46 Phe-α (m, 1H), 4.40 Pro-α (m, 1H), 4.09 Val-α (m, 1H), 3.68 Pro-δ (m, 1H), 3.59 Pro-δ (m, 1H), 3.14 Phe-β (m, 1H), 2.78 Phe-β (m, 1H), 2.04 Pro-β (m, 1H), 1.84 Ac-cap, Pro-β, Pro–γ & Val-β (m, 7H), 1.20 Ala-β (d, 3H, J = 6.9 Hz), 0.58 Val-γ (dd, 6H).

^{1}H NMR (10% D_2O/90% H_2O) δ: 8.68 Phe-NH (d, 1H, J = 7.9 Hz), 8.41 Ala-NH (d, 1H, J = 5.4 Hz), 8.30 Val-NH (d, 1H, J = 7.9 Hz), 7.68 Cap-NH (s, 1H), 7.33 Phe-ring (m, 2H), 7.30 Phe-ring (m, 3H), 7.26 Cap-NH (s, 1H), 4.65 Phe-α (m, 1H), 4.54 Ala-α (m,1H), 4.46 Pro-α (m,

. 1H), 4.08 Val-α (m, 1H), 3.83 Pro-δ (m, 1H), 3.66 Pro-δ (m, 1H), 3.30 Phe-β (m, 1H), 2.94 Phe-β (m, 1H), 2.32 Pro-β (m, 1H), 2.02 Pro-γ (m, 2H), 1.99 Ac-cap (s, 3H), 1.92 Pro-β (m, 1H), 1.88 Val-β (m, 1H), 1.35 Ala-β (d, 3H), 0.69 Val-γ (d, 3H), 0.60 Val-γ (d, 3H).

^{13}C NMR (DMSO-d_6) δ: 173.0, 171.5, 171.0, 170.5, 168.7, 138.2, 129.0, 127.9, 126.0, 59.5, 57.6, 54.0, 46.6, 45.9, 37.2, 29.9, 29.0, 24.4, 22.1, 19.0, 17.3, 17.0.

Calc. for $[MH]^+$ $C_{24}H_{36}N_5O_5$ [474.2716]; Obs. [474.2716]. TLC (A) R_f = 0.75.

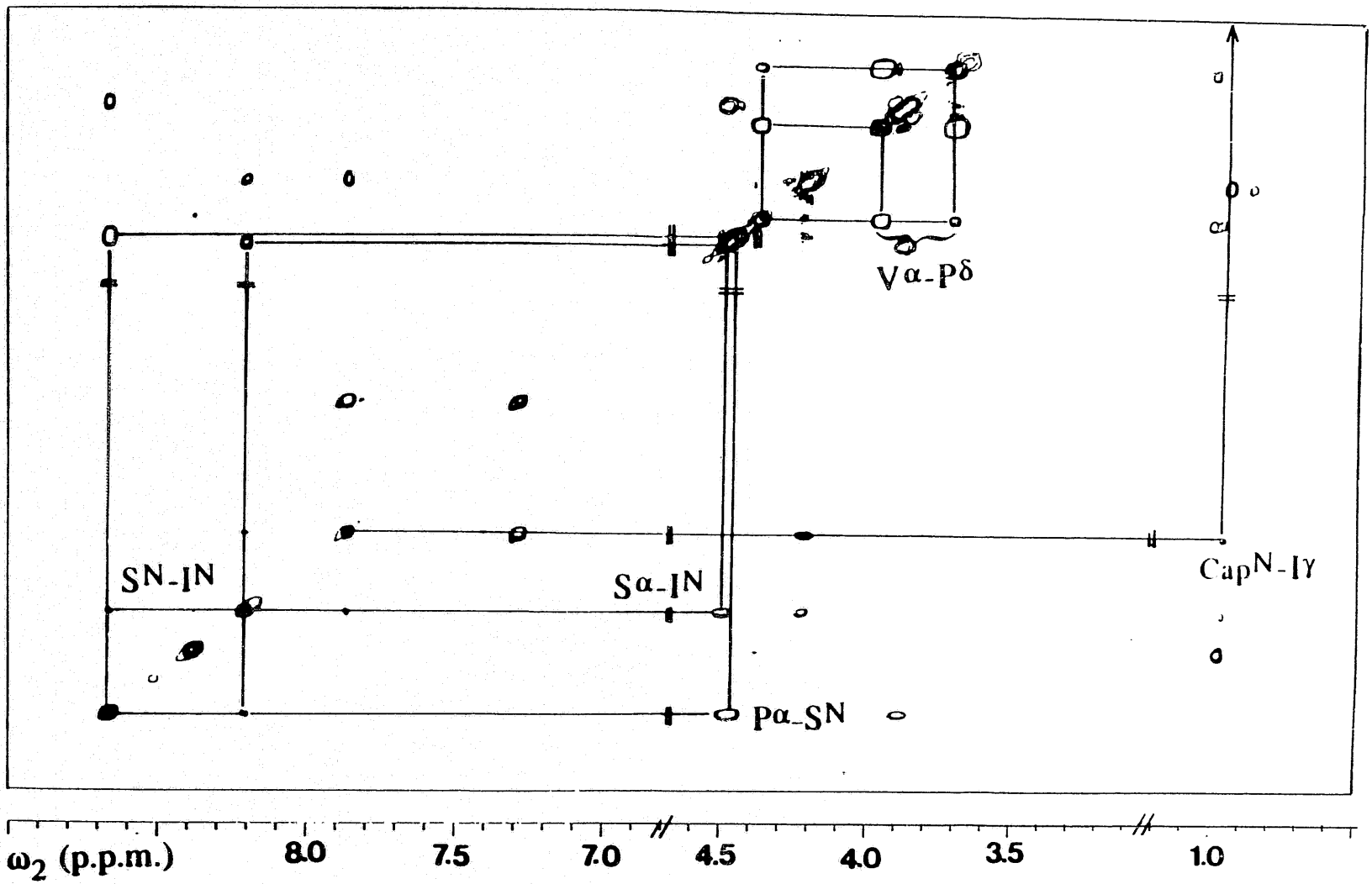
Ac-Ala-Pro-D-Leu-Phe-NH$_2$

^{1}H NMR (DMSO-d_6) δ: 8.15 Ala-NH (d, 1H, J = 7.6 Hz), 8.12 Phe-NH (d, 1H, J = 8.8 Hz), 7.95 Leu-NH (d, 1H, J = 8.0 Hz), 7.34 Cap-NH (s, 1H), 7.24 Phe-ring (m, 5H), 7.16 Cap-NH (s, 1H), 4.55 Ala-α (m, 1H), 4.39 Phe-α (m, 1H), 4.27 Pro-α (m, 1H), 4.17 Leu-α (m, 1H), 3.63 Pro-δ (m, 2H), 3.12 Phe-β (m, 1H), 2.81 Phe-β (m, 1H), 2.04 Pro-β (m, 1H), 1.94 Pro-γ (m, 1H), 1.88 Pro-γ (m, 1H), 1.83 Ac-cap (s, 3H), 1.75 Pro-β (m, 1H), 1.30 Leu-β (m, 2H), 1.20 Ala-β (d, 3H, J = 7.0 Hz), 0.85 Leu-γ (m, 1H), 0.78 Leu-δ (d, 3H, J = 5.7 Hz), 0.74 Leu-δ (d, 3H, J = 5.6 Hz).

^{1}H NMR (10% D_2O/90% H_2O) δ: 8.63 Phe-NH (d, 1H, J = 8.3 Hz), 8.44 Leu-NH (d, 1H), 8.42 Ala-NH (d, 1H), 7.73 Cap-NH (s, 1H), 7.41 Phe-ring (m, 2H), 7.36 Phe-ring (m, 1H), 7.32 Phe-ring & Cap-NH (m, 3H) 4.68 Phe-α (m, 1H), 4.60 Ala-α (m, 1H), 4.43 Pro-α (m, 1H), 4.25 Leu-α (m, 1H), 3.85 Pro-δ (m, 1H), 3.70 Pro-δ (m, 1H), 3.40 Phe-β (m, 1H), 2.95 Phe-β (m, 1H), 2.30 Pro-β (m, 1H) 2.05, Pro-γ (m, 2H), 2.02 Ac-cap (s, 3H), 1.90 Pro-β (m, 1H), 1.38 Ala-β (d, 3H), 1.32 Leu-β (m, 2H), 1.25 Leu-γ (m, 1H), 0.82 Leu-δ (d, 3H), 0.79 Leu-δ (d, 3H).

^{13}C NMR (DMSO-d_6) δ: 173.0, 171.7, 171.5, 171.1, 168.7, 138.2, 129.1, 127.9, 126.0, 59.8, 54.1, 51.0, 46.8, 46.0, 37.2, 29.0, 24.5, 23.9, 22.8, 22.2, 21.6, 16.9.

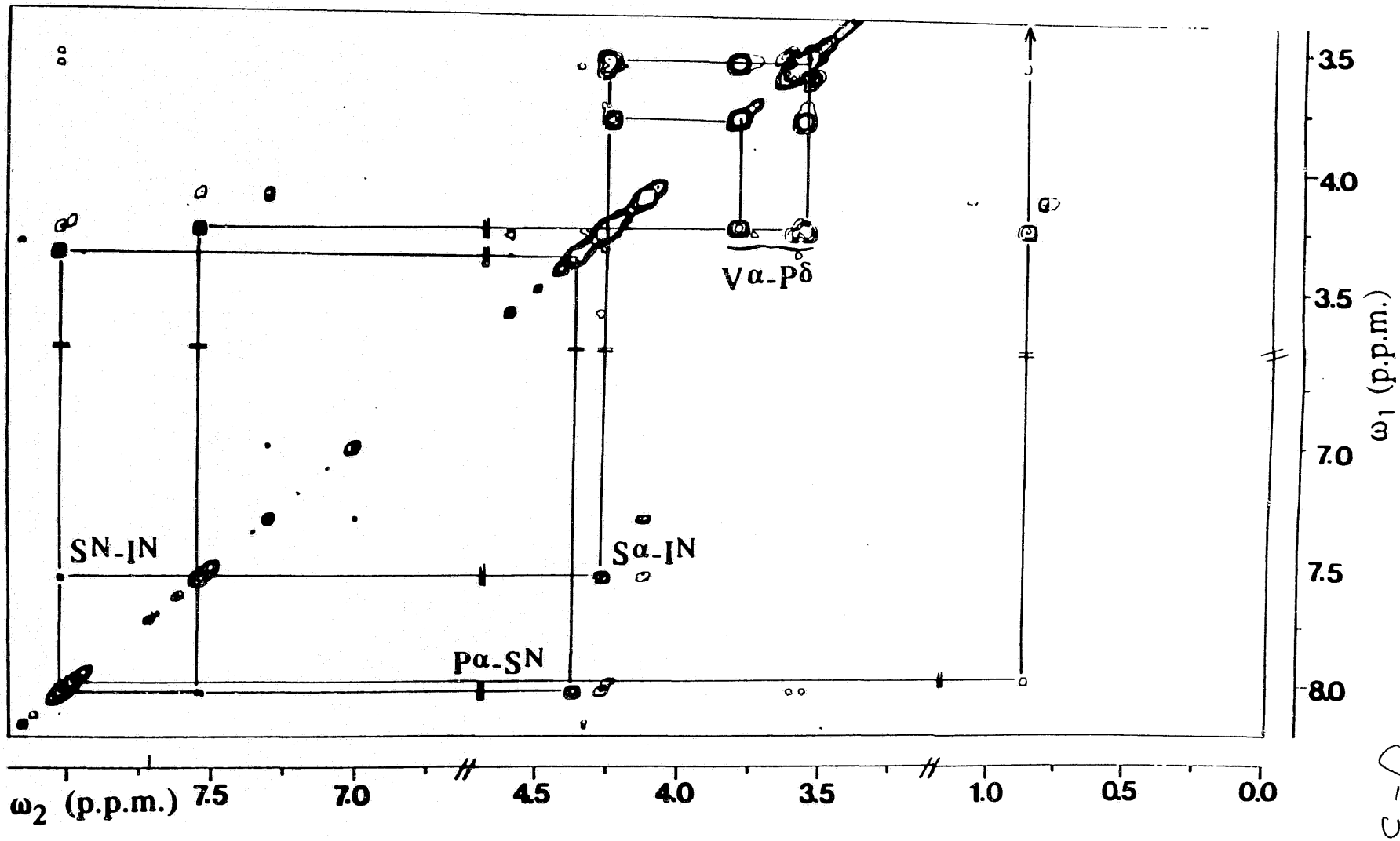
Calc. for $[MNa]^+$ $C_{25}H_{37}NaN_5O_5$ [510.2692]; Obs. [510.2690]. TLC (A) R_f = 0.60.



ROESY OF Ac-Val-Pro-D-Ser-Ile-NH_2

in D_2O/H_2O

J-31-88-117



ROESY OF Ac-Val-Pro-D-Ser-Ile-NH_2

in DMSO

J-318-84-NH